Carbohydrate Research, 199 (1990) 139–151
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Glycosides of 1-amino-1-deoxy-D-fructose*†

M. de Gracia García Martín, Consolación Gasch, and Antonio Gómez-Sánchez‡
Instituto de la Grasa y sus Derivados, C.S.I.C., and Departamentos de Química Orgánica and Química Orgánica y Farmacéutica, Universidad de Sevilla, Apartado de Correos No. 553, 41071 Seville (Spain)

(Received August 2nd, 1989; accepted for publication, October 7th, 1989)

ABSTRACT

A general procedure for the preparation of alkyl 1-amino-1-deoxy-α-D-fructofuranosides is described. 1-Amino-1-deoxy-D-fructose (acetate salt) was transformed into several *N*-[1-(2-acylvinyl)]- and *N*-[1-(2,2-diacylvinyl)] derivatives. Fischer glycosidation of these compounds with various alcohols yielded mixtures of the corresponding alkyl α- and β-D-fructofuranosides in which the α anomers preponderated (35–60%). *N*-Deprotection of the latter compounds afforded the alkyl 1-amino-1-deoxy-α-D-fructofuranosides in yields of 75–95%.

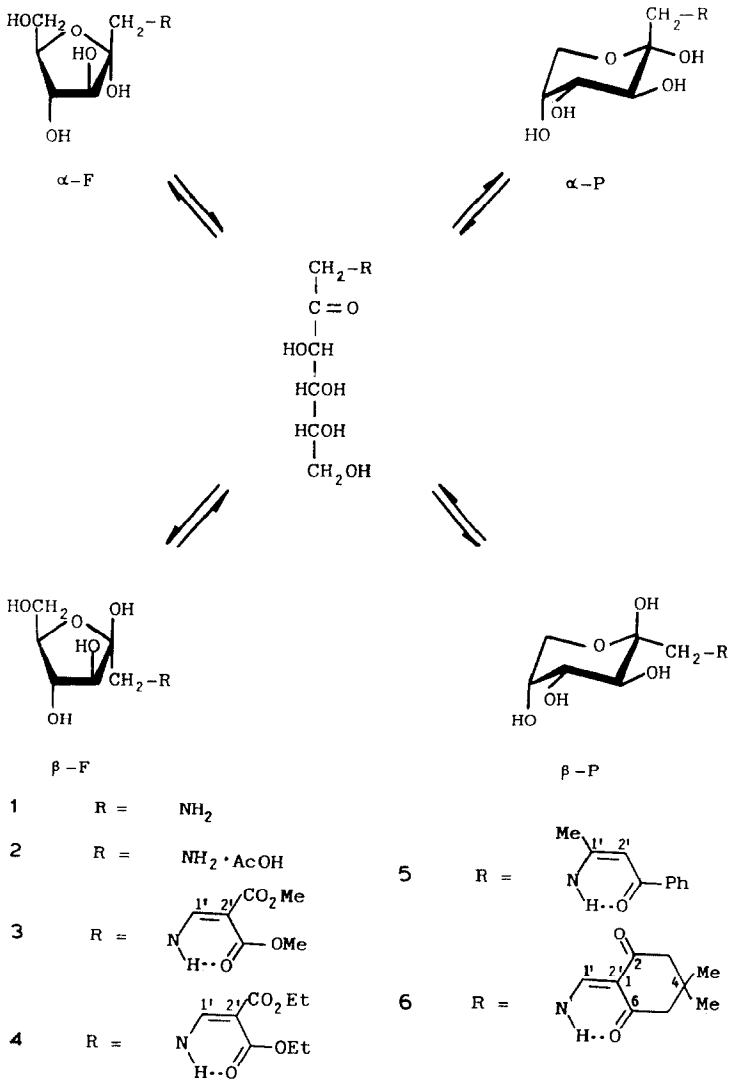
INTRODUCTION

We have demonstrated[1,2] the utility of the 2-acylvinyl and 2,2-diacylvinyl groups for protecting the amino function of 2-amino-2-deoxy-D-glucose during acetylation and glycosidation reactions. The advantages of these protecting groups are the easy preparation, in high yields, of the *N*-protected derivatives, their stability, and the selective and easy removal of the *N*-protecting group under mild conditions. Similar *N*-protection of other amino sugars is feasible, and several *O*-acylated glycosylamines with an unsubstituted NH_2 group have been prepared[3] by this procedure.

1-Amino-1-deoxy-D-fructose (**1**) and some of its *N*-derivatives (the "Amadori compounds") are of interest because of their involvement in some biological processes[4] and in the non-enzymic browning of foods[5]. However, little of the chemistry of these amino sugars is known, which is due probably to the lack of suitable *N*-protected derivatives of **1**. The preparation of a few *N*-protected derivatives of **1**, and the transformation of one of them (**3**) into methyl 1-amino-1-deoxy-α-D-fructofuranoside has been described[6]. However, Fischer glycosidation of **3** with alcohols other than MeOH is accompanied by partial transesterification that results in the formation of a complex mixture of products. In order to overcome this limitation, the *N*-protected derivatives **4**–**6** of **1** have been prepared and their Fischer glycosidation with various alcohols investigated.

* Presented at the IVth European Symposium on Carbohydrates, Darmstadt, F.R.G., July 17–21, 1987.
† Protection of the Amino Group of Amino Sugars by the Acylvinyl Group, Part VI. For Part V, see ref. 1.
‡ Author for correspondence.

0008-6215/90/$ 03.50



RESULTS AND DISCUSSION

1-Deoxy-1-[(2,2-diethoxycarbonylvinyl)amino]-D-fructose (**4**) was obtained (~ 100%) by treatment of the acetate salt (**2**) of **1** with ethyl 3-ethoxy-2-ethoxycarbonylacrylate in water in the presence of sodium carbonate. The known[7] 1-[(2-benzoylvinyl)-amino]-1-deoxy-D-fructose (**5**) was prepared (87%) by treatment of **2** with 1-phenyl-1,3-butanedione in methanol but, in the presence of triethylamine[7], the yield was lower, and the product was contaminated substantially by pyrrole compounds resulting from its cyclization. The derivative **6** was prepared[6] by the transamination reaction between **1** and 5,5-dimethyl-2-phenylaminomethylene-1,3-cyclohexanedione.

Compound **4** had u.v. and i.r. absorptions, and ^{1}H- and ^{13}C-n.m.r. signals (see Experimental), characteristic of an intramolecularly bonded *N*-substituted 3-aminomethylenemalonic ester[8]. Compounds **4** and **5** mutarotated, the equilibria being reached in 4 days. The ^{13}C-n.m.r. spectra of freshly prepared solutions of **4** and **5**, either in D_2O or $(CD_3)_2SO$, revealed only the β-D-pyranose form in the $^2C_5$ conformation. These results suggest that, in the solid state, **4** and **5** have this structure. However, at equilibrium, the ^{13}C-n.m.r. spectra of **4** and **5** indicated the presence of up to three components, namely, the α- and the β-D-furanose forms and the β-D-pyranose form. The assignment of the signals of the sugar moiety (Table I) for each of the isomeric forms of **4** and **5** was made by comparison with those for **2** and for other 1-deoxy-1-[(2,2-diacylvinyl)amino]-D-fructoses[2]. The data in Table II show that the positions of the equilibria depended on the solvent. For solutions in D_2O, the equilibria are shifted to the β-D-pyranose form, whereas the α-D-furanose form is favoured in $(CD_3)_2SO$.

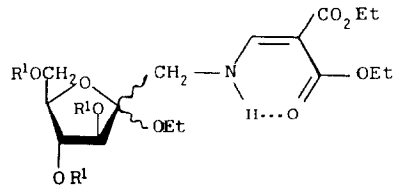
Fischer glycosidation of **4**–**6** with various alcohols gave α,β-mixtures of the alkyl D-fructofuranosides (43–80% overall yield). The α-glycoside (**7α**, **9α**, **11α**, **13α**, **15α**, and **17α**) were the main products (35–62%), and the β-glycosides (**7β**, **9β**, **11β**, **13β**, **15β**, and

TABLE I

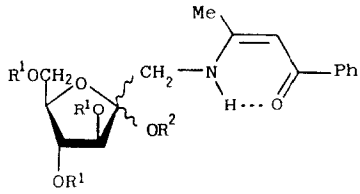
^{13}C-N.m.r. data[a,b] (δ, p.p.m.) for compounds **4** and **5**

Atom	**4**			**5**		
	β-P	*β-F*	*α-F*	*β-P*	*β-F*	*α-F*
C-1	55.92 (55.29)	54.45 (54.00)	54.60 (54.51)	48.56 (48.90)	48.40 (47.91)	48.40 (47.81)
C-2	97.97 (97.18)	101.30 (100.93)	104.52 (103.60)	97.39 (97.81)	97.39 (101.53)	97.39 (104.54)
C-3	70.43 (69.66)	77.28 (77.24)	81.86 (81.44)	69.44 (69.89)	76.15 (76.99)	76.36 (81.69)
C-4	69.96 (69.13)	76.92 (74.84)	75.01 (76.95)	68.83 (69.19)	74.00 (74.88)	74.65 (76.90)
C-5	69.90 (69.13)	81.82 (85.52)	83.42 (83.39)	68.70 (68.84)	80.80 (82.55)	81.15 (82.99)
C-6	64.62 (63.88)	63.56 (62.94)	63.10 (62.29)	63.43 (63.82)	62.23 (62.96)	62.03 (62.43)
C-1′	162.56 (161.12)	162.35 (161.05)	162.46 (161.12)	168.31 (165.55)	(165.48)	
C-2′	89.48 (88.62)	89.14 (88.84)	89.75 (88.19)	98.72 (91.63)	(91.34)	

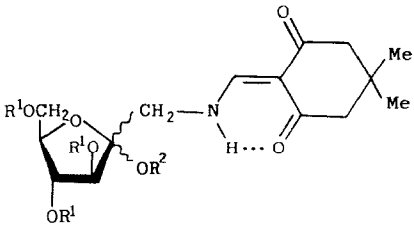
[a] At 50.3 MHz in D_2O. [b] In brackets, in $(CD_3)_2SO$.



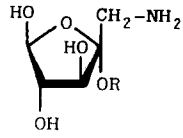
7 α,β R^1 = H
8 α,β R^1 = Ac



9 α,β R^1 = H R^2 = Me
10 β R^1 = Ac R^2 = Me
11 α,β R^1 = H R^2 = Allyl
12 α R^1 = Ac R^2 = Allyl



13 α,β R^1 = H R^2 = Me
14 β R^1 = Ac R^2 = Me
15 α,β R^1 = H R^2 = Allyl
16 α,β R^1 = Ac R^2 = Allyl
17 α,β R^1 = H R^2 = Bn
18 α R^1 = Ac R^2 = Bn



19 R = Et
20 R = Me
21 R = Allyl
22 R = Bn

17β) were isolated in yields of 3–7%. The reactions with **6** were faster than those[4] of the analogous derivative of 2-amino-2-deoxy-D-glucose, and the glycosides were obtained in higher yields.

The structures of the new glycosides were established on the basis of their analytical and spectral data, and, for most of the compounds, on those of their triacetates (see Experimental and Table III). The assignments of the ^{13}C-n.m.r. spectra were made by comparison with those for **4** and **5** (Table I) and **6**[6]. The chemical shifts of the resonances of the carbons of the sugar ring (Table III) and, especially the high δ values observed for those of C-2,5 for each compound, indicated the furanose structure; these δ values were higher for the α anomer than for the β anomer. The anomeric configurations were confirmed by the $[\alpha]_D$ and $J_{3,4}$ values (2.1–2.7 Hz for the α anomers, 6.9–7.9 Hz for the β anomers) in accordance with the values observed for (D-fructos-1-yl)amino acids and other Amadori compounds[6,9].

Removal of the *N*-protecting group of **7***a*, **9***a*, **13***a*, **15***a*, and **17***a* was achieved easily by hydrolysis in aqueous acetone in the presence of Amberlite IRA-400 (HO^-) resin at room temperature[2,6]. The corresponding alkyl 1-amino-1-deoxy-α-D-fructo-

TABLE II

Percentage[a] of the isomers of **4** and **5** in D_2O and (in brackets) in $(CD_3)_2SO$ at equilibrium

Compound	*Isomer*		
	β-P	*β-F*	*α-F*
4	74 (25)	15 (25)	11 (50)
5	55 (25)	20 (25)	25 (50)

[a] At 20°.

furanosides (**19–22**) were isolated in good yields. The physical constants, yields, and analytical data appear in Table IV and the ^{13}C-n.m.r. data in Table V.

The above results reveal an easy route to the hitherto unknown alkyl 1-amino-1-deoxy-α-D-fructofuranosides and further illustrate the utility of the 2-acylvinyl and 2,2-diacylvinyl groups in amino sugar chemistry.

TABLE III

^{13}C-N.m.r. data[a] (δ, p.p.m.) for compounds **7α–9α**, **11α–13α**, **15α–18α**, **7β–11β**, and **13β–17β**.

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
7α[b]	46.40	108.40	79.73	78.00	86.34	61.56
8α[c]	49.25	106.41	79.93	77.47	80.80	62.69
7β[b]	50.62	102.31	76.01	78.67	81.67	63.33
8β[c]	51.77	103.17	76.00	74.72	77.50	64.09
9α[b]	44.03	107.59	80.28	77.29	83.52	62.23
9β[b]	45.35	103.38	77.98	74.48	82.34	62.45
10β[c]	45.70	103.98	77.32	75.68	78.40	64.65
11α[b]	44.76	107.67	80.89	77.11	83.33	62.18
12α[b]	42.70	106.43	79.78	76.90	80.39	62.47
11β[b]	45.66	103.43	77.68	74.34	82.32	62.40
13α[b]	50.79	106.54	80.62	76.55	82.66	61.54
13β[b]	51.20	108.03	78.89	75.55	81.90	63.09
14β[c]	51.93	108.31	76.23	74.63	78.05	64.29
15α[b]	51.13	107.86	81.07	77.70	85.24	62.72
16α[c]	51.36	107.91	80.58	77.05	80.95	62.25
15β[b]	53.23	108.13	79.11	75.23	82.64	62.31
16β[c]	52.58	108.05	76.15	74.51	77.89	63.98
17α[b]	51.39	106.87	81.77	76.97	83.07	61.74
18α[c]	49.57	107.27	80.31	76.89	80.46	62.24
17β[b]	52.53	107.09	78.31	74.03	82.10	61.86

[a] At 50.3 MHz. [b] In $(CD_3)_2SO$. [c] In $CDCl_3$.

TABLE IV

Data on **19**–**22**

Compound	$[\alpha]_D^{25}$ (*water*) (*degrees*)	*M.p.* (*degrees*)	*Yield* (%)	*Elemental analysis*					
				Calc.			*Found*		
				C	*H*	*N*	*C*	*H*	*N*
19	+58		95	46.37	8.27	6.76	46.08	7.95	6.46
20[a]	+59	146–147	90[b] 76[c]						
21[d]	−94	140 (dec.)	75[c]	42.72	6.19	4.53	42.58	6.29	4.48
22	+34		87	57.98	7.11	5.20	57.45	7.25	4.84

[a]As its oxalate. Lit. m.p. 144–146°, $[\alpha]_D^{25}$ +59° (water). [b]From **13***a*. [c]From **9***a*. [d]As its oxalate. [e]From **15***a*.

EXPERIMENTAL

General methods. — Evaporations were conducted *in vacuo* at <40° (bath). Melting points were determinated with a Buchi melting-point apparatus and are uncorrected. Elemental analyses were carried out at the Instituto de Química Orgánica General, C.S.I.C. (Madrid) and the Departamento de Química Analítica, Facultad de Química, Universidad de Sevilla. Optical rotations were measured at room temperature with a Perkin–Elmer 241Mc polarimeter, u.v. spectra with a Hewlett–Packard 8450A spectrophotometer, and i.r. spectra (KBr pellets or solutions in $CHCl_3$) with a Perkin Elmer 1310 spectrophotometer. N.m.r. spectra were recorded for solutions in D_2O, $(CD_3)_2SO$, and CD_3Cl (internal Me_4Si), using a Varian XL-200 spectrometer. T.l.c. was

TABLE V

^{13}C-N.m.r. data[a,b] (δ, p.p.m.) for compounds **19**, **21** and **22**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OR*	$C_2O_4H_2$
19	42.86	107.19	82.01	77.00	82.21	60.82	55.81 15.93	
21	40.62	98.55	69.02	68.83	69.90	64.85	134.97 115.91 60.82	165.03
22	43.50	108.31	82.59	77.68	83.12	61.25	139.52 128.57 127.89 127.53 62.76	

[a]At 50.3 MHz. [b]In $(CD_3)_2SO$.

performed on Kieselgel 60 F_{254} (Merck) with detection by u.v. light or by charring with sulfuric acid. Silica Gel 60 (Merck) was used for column chromatography. Acetates were prepared conventionally by treating a cooled solution of the substrate in pyridine with excess of acetic anhydride for 2 h at room temperature.

*1-Deoxy-1-[(2,2-diethoxycarbonylvinyl)amino]-*D*-fructose (**4**).* — To a stirred solution of **2** (2.39 g, 10.0 mmol) and Na_2CO_3 (0.53 g, 5.0 mmol) in H_2O (7.5 mL) was added ethyl 3-ethoxy-2-ethoxycarbonylvinylacrylate (2.71 g, 12.0 mmol), and stirring was continued for 5 h. The solution was then concentrated and the syrupy residue was treated with Et_2O to give homogeneous (t.l.c.) amorphous **4** (3.15 g, 98%). After column chromatography, the analytical sample had $[\alpha]_D^{26}$ −19° (*c* 1, ethanol); λ_{max}^{EtOH} 226 and 279 nm (log ε 4.11 and 4.39); ν_{max}^{KBr} 1720s, 1680s, and 1630sh,s (C=O), and 1605sh,s cm^{-1} (C=C–NH). The ^{13}C-n.m.r. data are listed in Table I.

Anal. Calc. for $C_{14}H_{23}NO_9$: C, 48.13; H, 6.64; N, 4.01. Found: C, 47.77; H, 6.86; N, 4.22.

*1-[(2-Benzoyl-1-methylvinyl)amino]-1-deoxy-*D*-fructose (**5**).*– A suspension of 1-phenyl-1,3-butanedione (2.03 g, 13.0 mmol) and **2** (3.00 g, 12.0 mmol) in MeOH (50 mL) was boiled under reflux for 2 h, then concentrated until crystallization occurred, and refrigerated. The product was recrystallized from MeOH to give **5** (4.81 g, 87%), m.p. 110–112° [lit.[7] m.p. 114–115°, $[\alpha]_D^{23}$ +39.5° (*c* 1, methanol); λ_{max}^{EtOH} 243 nm (log ε 3.96); ν_{max}^{KBr} 1600 vs and 1580 s cm^{-1} (C=O and C=C–NH). The ^{13}C-n.m.r. data are listed in Table I.

Fischer glycosidation of the N*-acylvinyl derivatives* **4–6**. — A solution of the *N*-protected derivative (12 mmol) in the appropriate alcohol (100 mL) containing HCl (1.25% for MeOH and EtOH, and 0.75% for $CH_2=CHCH_2OH$ and BnOH) was heated at 65° under argon for 10–25 min (except for **4**, which reacted at room temperature in 90 min). Each mixture was then stirred with $2PbCO_3$. $Pb(OH)_2$, filtered, and concentrated to dryness. Column chromatography (CH_2Cl_2–MeOH) of the residue gave the corresponding alkyl α- and β-D-fructofuranoside.

Glycosidation of **4** with EtOH afforded **7***α* and **7***β*. Ethyl 1-deoxy-1-[(2,2-diethoxycarbonylvinyl)aminol-α-D-fructofuranoside (**7***α*), isolated as a syrup (60%), had $[\alpha]_D^{20}$ +40° (*c* 1.5, methanol); λ_{max}^{EtOH} 223 and 280 nm (log ε 4.07 and 4.34); $\nu_{max}^{CCl_4}$ 1710m, 1675s, 1655s, and 1635s (C=O), and 1610s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 9.20 (m, 1 H, NH), 7.89 (d, 1 H, $J_{NH,CH=}$ 14.2 Hz, =CH), 4.21 and 4.17 (2 q, each 2 H, 2 $COOCH_2CH_3$), 1.32 and 1.28 (2 t, each 3 H, 2 $COOCH_2CH_3$), and 1.22 (t, 3 H, OCH_2CH_3); ^{13}C, δ 168.93 and 166.56 (2 C=O), 160.58 (C-1′), 89.53 (C-2′), 59.83 and 59.79 (2 $COOCH_2CH_3$), 56.80 (OCH_2CH_3), 15.36 (OCH_2CH_3), and 14.16 and 14.08 (2 $COOCH_2CH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{16}H_{27}NO_9$: C, 50.92; H, 7.21; N, 3.71. Found: C, 51.03; H, 7.27; N, 3.73.

The corresponding 3,4,6-triacetate **8***a* (84%) had m.p. 87–89° (from EtOH), $[\alpha]_D^{26}$ +42° (*c* 1, chloroform); ν_{max}^{EtOH} 219 and 279 nm (log ε 4.14 and 4.40); ν_{max}^{KBr} 1760s, 1745s, and 1730s (C=O, AcO), 1680s, 1635s, and 1625s (C=O), and 1600s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$): ^1H, δ 9.25 (m, 1 H, $J_{NH,1'}$ 6.9, $J_{NH,1}$ 6.9 Hz, NH) 7.23 (d, 1 H,

$J_{NH,CH=}$ 14.7 Hz, =CH), 5.24 (d, 1 H, $J_{3,4}$ 2.7 Hz, H-3), 4.99 (dd, 1 H, $J_{4,5}$ 5.3 Hz, H-4), 4.40 (dd, 1 H, $J_{5,6'}$ 5.4, $J_{6,6'}$ −13.8 Hz, H-6'), 4.20 (m, 2 H, H-5,6), 4.24 and 4.18 (2 q, each 2 H, 2 $COOCH_2CH_3$), 3.60 (m, 4 H, H-1,1' and OCH_2CH_3), 2.18 and 2.09 (2 s, 9 H, 3 Ac), 1.33 (t, 3 H, OCH_2CH_3), and 1.26 and 1.25 (2 t, each 3 H, $COOCH_2CH_3$); ^{13}C, δ 170.52, 169.95, and 169.20 (3 $COCH_3$), 168.88 and 163.90 (2 COOEt), 160.30 (C-1'), 90.65 (C-2'), 59.86 and 59.63 (2 $COOCH_2CH_3$), 56.97 (OCH_2CH_3), 20.63 (3 $COCH_3$), 15.38 (OCH_2CH_3), and 14.44 and 14.32 (2 $COOCH_2CH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{22}H_{33}NO_{12}$: C, 52.48; H, 6.61; N, 2.78. Found: C, 52.70; H, 6.71; N, 2.78.

Ethyl 1-deoxy-1-[(2,2-diethoxycarbonylvinyl)aminol]-β-D-fructofuranoside (**7**β), isolated as a syrup (7%), had $[\alpha]_D^{19}$ ~0° (*c* 1.3, ethanol); λ_{max}^{EtOH} 228 and 281 nm (log ε 3.40 and 4.16); ν_{max}^{KBr} 1715s, 1675s, 1655s, and 1635vs (C=O), and 1610sh,s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 9.13 (m, 1 H, NH), 7.95 (d, 1 H, $J_{NH,CH=}$ 14.0 Hz, =CH), 4.21 and 4.17 (2 q, each 2 H, $COOCH_2CH_3$), 4.10 (m, 1 H, H-4), 3.92 (d, 1 H, $J_{3,4}$ 7.9 Hz, H-3), 1.32 and 1.28 (2 t, each 3 H, $COOCH_2CH_3$), and 1.18 (t, 3 H, OCH_2CH_3); ^{13}C, 169.10 and 166.76 (2 C=O), 160.63 (C-1'), 90.70 (C-2'), 60.10 and 60.03 (2 $COOCH_2CH_3$), 57.24 (OCH_2CH_3), 15.52 (OCH_2CH_3), and 14.36 and 14.26 (2 $COOCH_2CH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{16}H_{27}NO_9$: C, 50.92; H, 7.21; N, 3.71. Found: C, 50.39; H, 7.60; N, 3.47.

The corresponding 3,4,6-triacetate **8**β (77%) was a syrup and had $[\alpha]_D^{26}$ −36° (*c* 1, chloroform); λ_{max}^{EtOH} 205 and 279 nm (log ε 4.04 and 4.00); ν_{max}^{KBr} 1740vs (C=O, AcO), 1680s and 1655s (C=O), and 1605s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$); ^1H, δ 9.40 (m, 1 H, NH), 8.03 (d, 1 H, $J_{NH,CH=}$ 12.6 Hz, =CH), 5.45 (dd, 1 H, $J_{4,5}$ 6.3 Hz, H-4), 5.13 (d, 1 H, $J_{3,4}$ 7.3 Hz, H-3), 4.34 (dd, 1 H, H-6'), 4.28 and 4.18 (2 q, each 2 H, 2 $COOCH_2CH_3$), 4.19 (dd, 1 H, $J_{6,6'}$ −8.0 Hz, H-6), 4.07 (dt, 1 H, $J_{5,6}$ 6.5, $J_{5,6'}$ 3.8 Hz, H-5), 3.6 (m, 2 H, H-1,1'), 2.14, 2.10, and 2.08 (3 s, each 3 H, 3 Ac), 1.35 (t, 3 H, OCH_2CH_3), and 1.30 and 1.21 (2 t, each 3 H, 2 $COOCH_2CH_3$); ^{13}C, δ 170.56, 170.26, and 169.82 (3 $COCH_3$), 168.65 and 165.86 (2 COOEt), 160.41 (C-1'), 90.76 (C-2'), 59.62 and 59.44 (2 $COOCH_2CH_3$), 57.48 (OCH_2CH_3), 20.38 and 20.49 (3 $COCH_3$), 15.13 (OCH_2CH_3), and 14.18 and 14.12 (2 $COOCH_2CH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{22}H_{33}NO_{12}$: C, 52.48; H, 6.61; N, 2.78. Found: C, 52.18; H, 6.58; N, 2.80.

Glycosidation of **5** with MeOH gave **9**α and **9**β. Methyl 1-[(2-benzoyl-1-methylvinyl)amino]-1-deoxy-α-D-fructofuranoside (**9**α, 40%) had m.p. 147–148° (from MeOH) $[\alpha]_D^{26}$ + 104° (*c* 0.5 methanol); λ_{max}^{EtOH} 243 and 344 nm (log ε 3.95 and 4.34); ν_{max}^{KBr} 1600 vs (C=O) and 1580s cm^{-1} (C=C–NH). N.m.r. data [$(CD)_3)_2SO$]: ^1H, δ 11.30 (t, 1 H, $J_{NH,1}$ 6.0, $J_{NH,1'}$ 6.0 Hz, NH), 7.43 and 7.34 (2 m, 5 H, Ph), 5.75 (s, 1 H, =CH), 3.48 (s, 3 H, OMe), and 2.11 (s, 3 H, CH_3); ^{13}C, δ 185.48 (C=O), 165.44 (C-1'), 140.33, 130.56, 128.38, and 126.79 (C_6H_5), 91.51 (C-2'), 48.55 (OCH_3), and 19.65 (CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{17}H_{23}NO_6$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.30; H, 6.69; N, 3.99.

Methyl 1-[(2-benzoyl-1-methylvinyl)amino]-1-deoxy-*β*-D-fructofuranoside (**9***β*, 4%) had m.p. 167–168° (from MeOH), $[\alpha]_D^{19}$ +24° (*c* 0.7, ethanol); ν_{max}^{KBr} 1600s (C=O) and 1580s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 11.40 (t, 1 H, $J_{NH,1}$ 6.0, $J_{NH,1'}$ 6.0 Hz, NH), 7.96 and 7.55 (2 m, 5 H, Ph), 5.91 (s, 1 H, =CH), 3.40 (s, 3 H, OMe), and 2.21 (s, 3 H, CH_3); ^{13}C, δ 185.94 (C=O), 165.82 (C-1'), 140.16, 130.78, 128.49, and 126.88 (C_6H_5), 91.87 (C-2'), 49.18 (OCH_3), and 19.52 (CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{17}H_{23}NO_6$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.52; H, 7.10; N, 4.05.

The corresponding 3,4,6-triacetate **10***β* (90%) had m.p. 128–130° (from EtOH), $[\alpha]_D^{19}$ −59° (*c* 1, chloroform); λ_{max}^{EtOH} 243 and 341 nm (log ε 3.97 and 4.31); ν_{max}^{KBr} 1735s (C=O, AcO), 1600s (C=O), and 1580s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$); ^1H, δ 11.50 (t, 1 H, $J_{NH,1}$ 5.9, $J_{NH,1'}$ 5.9 Hz, NH), 7.89 and 7.41 (2 m, 5 H, Ph), 5.73 (s, 1 H, =CH), 5.41 (d, 1 H, $J_{3,4}$ 7.5 Hz, H-3), 5.36 (dd, 1 H, $J_{4,5}$ 5.4, H-4), 4.39 (dd, 1 H, $J_{5,6'}$ 6.1, $J_{6,6'}$ −11.7 Hz, H-6'), 4.24 (dd, 1 H, $J_{5,6}$ 2.2 Hz, H-6), 3.43 (s, 3 H, OMe), 2.12, 2.11, and 2.10 (3 s, each 3 H, 3 Ac), and 2.03 (s, 3 H, CH_3); ^{13}C, δ 189.37 (C=O), 171.02 and 170.68 (3 $COCH_3$), 164.88 (C-1'), 140.69, 131.07, 128.58, and 127.44 (C_6H_5), 93.53 (C-2'), 49.98 (OCH_3), 21.25, 21.19, and 21.15 (3 $COCH_3$), and 20.11 (CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{23}H_{29}NO_9$: C, 59.69; H, 6.31; N, 3.02. Found: C, 59.69; H, 6.55; N, 3.35.

Glycosidation of **5** with $CH_2=CHCH_2OH$ afforded **11***α* and **11***β*. Allyl 1-[(2-benzoyl-1-methylvinyl)amino]-1-deoxy-*α*-D-fructofuranoside (**11***α*, 35%) had m.p. 120–122° (from EtOH), $[\alpha]_D^{19}$ +104° (*c* 1, ethanol); λ_{max}^{EtOH} 243 and 344 nm (log ε 3.94 and 4.32); ν_{max}^{KBr} 1600 vs (C=O) and 1580s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 11.31 (t, 1 H, $J_{NH,1}$ 6.2, $J_{NH,1'}$ 6.2 Hz, NH), 7.85 and 7.47 (2 m, 5 H, Ph), 5.97 (m, 1 H, $CH_2=CH$), 5.76 (s, 1 H, =CH), 5.35 and 5.16 (2 dd, each 1 H, $CH_2=CH$), and 2.11 (s, 3 H, CH_3); ^{13}C, δ 187.48 (C=O), 165.42 (C-1'), 140.31, 130.53, 128.36, and 126.77 (C_6H_5), 91.52 (C-2'), 135.67, 115.94, and 62.10 (allyl), and 19.65 (CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.49; H, 7.14; N, 3.91.

The corresponding 3,4,6-triacetate **12***α* (91%) was a syrup. N.m.r. data ($CDCl_3$): ^1H, δ 11.49 (t, 1 H, $J_{NH,1}$ 6.0, $J_{NH,1'}$ 6.0 Hz, NH), 7.85 and 7.39 (2 m, 5 H, C_6H_5), 5.95 (m, 1 H, $CH_2=CH$), 5.68 (s, 1 H, =CH), 5.38 and 5.19 (2 dd, each 1 H, $CH_2=CH$), 5.36 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 5.03 (dd, 1 H, $J_{4,5}$ 5.1 Hz, H-4), 4.47 (dd, 1 H, $J_{6,6'}$ −10.8 Hz, H-6'), 4.15 (m, 2 H, H-5,6), 3.70 (dd, 1 H, $J_{1,1'}$ −14.4 Hz, H-1'), 3.60 (dd, 1 H, H-1), 2.23 (s, 3 H, CH_3), and 2.09 and 2.06 (2 s, 9 H, 3 Ac); ^{13}C, δ 187.32 (C=O), 169.86, 169.27, and 168.64 (3 $COCH_3$), 163.09 (C-1'), 139.48, 129.69, 127.30, and 126.14 (C_6H_5), 133.22, 115.62, and 62.09 (allyl), 92.07 (C-2'), and 19.90 (CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{25}H_{31}NO_9$: C, 61.34; H, 6.38; N, 2.86. Found: C, 61.10; H, 6.10; N, 2.70.

Allyl 1-[(2-benzoyl-1-methylvinyl)amino]-1-deoxy-*β*-D-fructofuranoside (**11***β*, 7%) had m.p. 160–161° (from EtOH), $[\alpha]_D^{19}$ +20° (*c* 1, ethanol); λ_{max}^{EtOH} 243 and 344 nm (log *ε* 3.76 and 4.15), ν_{max}^{KBr} 1600s (C=O) and 1575s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, *δ* 11.32 (t, 1 H, $J_{NH,1}$ 6.0, $J_{NH,1'}$ 6.0 Hz, NH), 7.85 and 7.45 (2 m, 5 H, Ph), 5.91 (m, 1 H, CH_2=CH), 5.80 (s, 1 H, =CH), and 5.30 and 5.11 p.p.m. (2 dd, each 1 H, CH_2=CH).

Anal. Calc. for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.70; H, 7.04; N, 4.17.

Glycosidation of **6** with MeOH afforded **13***α* and **13***β*. Methyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-*α*-D-fructofuranoside (**13***α*, 62%) had m.p. 89–91° (from H_2O), $[\alpha]_D^{26}$ +31° (*c* 1, ethanol); λ_{max}^{EtOH} 253 and 305 nm (log *ε* 4.14 and 4.25); ν_{max}^{KBr} 1660vs and 1590vs (C=O), and 1570vs cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, *δ* 10.93 (dt, 1 H, NH), 8.05 (d, 1 H, $J_{NH,CH=}$ 14.4 Hz, =CH), 3.93 (d, 1 H, $J_{3,4}$ 5.5 Hz, H-3), 3.60 (m, 2 H, H-1,1'), 3.51 (dd, 1 H, $J_{4,5}$ 7.8 Hz, H-4), 3.32 (dd, 1 H, $J_{5,6}$ 6.4, $J_{6,6'}$ −11.9 Hz, H-6), 3.22 (s, 3 H, OMe), 2.28 and 2.23 (2 s, each 2 H, 2 CH_2), and 0.97 (s, 6 H, 2 CH_3); ^{13}C, *δ* 197.32 and 194.34 (2 C=O), 158.90 (C-1'), 106.06 (C-2'), 50.71 and 50.46 (2 CH_2), 48.27 (OCH_3), 30.63 (-C-), and 28.25 and 27.69 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{16}H_{25}NO_7 \cdot H_2O$: C, 53.18; H, 7.53; N, 3.88. Found: C, 53.31; H, 7.70; N, 3.84.

Methyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)aminol]-*β*-D-fructofuranoside (**13***β*, 5%) was a syrup, $[\alpha]_D^{20}$ ~0° (*c* 1, methanol); λ_{max}^{EtOH} 251 and 306 nm (log *ε* 4.12 and 4.25), ν_{max}^{KBr} 1660vs and 1590vs (C=O), and 1570s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, *δ* 11.07 (dt, 1 H, $J_{NH,1}$ 6.5, $J_{NH,1'}$ 6.5 Hz, NH), 8.12 (d, 1 H, $J_{NH,CH=}$ 14.1 Hz, =CH), 3.36 (s, 3 H, OMe), 2.36 and 2.33 (2 s, each 2 H, 2 CH_2), and 1.03 (s, 6 H, 2 CH_3); ^{13}C, *δ* 199.70 and 197.13 (2 C=O), 159.70 (C-1'), 101.95 (C-2'), 50.96 and 50.81 (2 CH_2), 49.14 (OCH_3), 31.19 (-C-), and 28.61 and 28.15 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.97; H, 7.34; N, 4.08. Found: C, 55.75; H, 7.10; N, 3.91.

The corresponding 3,4,6-triacetate **14***β* (87%) was a syrup, $[\alpha]_D^{26}$ −22° (*c* 1, chloroform); λ_{max}^{EtOH} 251 and 305 nm (log *ε* 4.00 and 4.10), ν_{max}^{KBr} 1745vs (C=O, AcO), 1665s and 1605vs (C=O), and 1585sh,s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$): ^1H, *δ* 11.32 (m, 1 H, NH), 8.12 (d, 1 H, $J_{NH,CH=}$ 14.7 Hz, =CH), 5.45 (dd, 1 H, $J_{3,4}$ 7.7, $J_{4,5}$ 6.2 Hz, H-4), 5.13 (d, 1 H, H-3), 4.36 (dd, 1 H, $J_{5,6'}$ 3.3, $J_{6,6'}$ −11.7 Hz, H-6'), 4.19 (dd, 1 H, $J_{5,6}$ 6.7 Hz, H-6), 4.09 (ddd, 1 H, H-5), 3.68 (dd, 1H, $J_{NH,1}$ 7.0, $J_{1,1'}$ −11.7 Hz, H-1), 3.53 (dd, 1 H, $J_{NH,1'}$ 6.1 Hz, H-1'), 3.37 (s, 3 H, OMe), 2.40 and 2.36 (2 s, each 2 H, 2 CH_2), 2.16, 2.11, and 2.07 (3 s, each 3 H, 3 Ac), and 1.06 (s, 6 H, 2 CH_3); ^{13}C, *δ* 199.40 and 196.36 (2 C=O), 171.01, 170.60, and 170.08 (3 $COCH_3$), 159.42 (C-1'), 102.94 (C-2'), 51.48 and 51.21 (2 CH_2), 49.63 (OCH_3), 31.18 (-C-), 28.71 and 28.55 (2 CH_3), and 20.86, 20.77, and 20.66 (3 $COCH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{22}H_{31}NO_{10}$: C, 56.28; H, 6.66; N, 2.98. Found: C, 56.20; H, 6.53; N, 2.75.

Glycosidation of **6** with $CH_2=CHCH_2OH$ gave **15***α* and **15***β*. Allyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-*α*-D-fructofuranoside (**15***α*, 51%) was amorphous, $[\alpha]_D^{26}$ +22° (*c* 1, ethanol); λ_{max}^{EtOH} 253 and 305 nm (log ε 4.12 and 4.24); $\nu_{max}^{CHCl_3}$ 1665s and 1600vs (C=O), and 1575sh,s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, *δ* 11.15 (dt, 1 H, $J_{NH,1}$ 6.5, $J_{NH,1'}$ 6.5 Hz, NH), 8.11 (d, 1 H, $J_{NH,CH=}$ 14.4 Hz, =CH), 5.93 (m, 1 H, $CH_2=CH$), 5.32 and 5.21 (2 dd, each 1 H, $CH_2=CH$), 2.36 and 2.32 (2 s, each 2 H, 2 CH_2), and 1.03 (s, 6 H, 2 CH_3); ^{13}C, *δ* 199.62 and 197.02 (2 C=O), 159.75 (C-1′), 134.01, 117.57, and 61.31 (allyl), 107.61 (C-2′), 50.87 and 50.56 (2 CH_2), 31.18 (-C-), and 28.52 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{18}H_{27}NO_7 \cdot H_2O$: C, 55.80; H, 7.55; N, 3.62. Found: C, 55.55; H, 7.38; N, 3.42.

The corresponding 3,4,6-triacetate **16***α* (94%) was a hygroscopic syrup, $[\alpha]_D^{26}$ +31° (*c* 1, ethanol); λ_{max}^{EtOH} 251 and 304 nm (log ε 4.10 and 4.20); $\nu_{max}^{CHCl_3}$ 1740vs (C=O, AcO), 1660s and 1595vs (C=O), and 1580sh,s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$): ^1H, *δ* 11.08 (dt, 1 H, NH), 8.01 (d, 1 H, $J_{NH,CH=}$ 13.8 Hz, =C*H*), 5.93 (m, 1 H, $CH_2=CH$), 5.38 and 5.23 (2 dd, each 1 H, $CH_2=CH$), 5.28 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 4.97 (dd, 1 H, $J_{4,5}$ 5.2 Hz, H-4), 4.20 (m, 3 H, H-5,6,6′), 3.74 (dd, 1 H, $J_{NH,1}$ 7.4, $J_{1,1'}$ −14.3 Hz, H-1), 3.61 (dd, 1 H, $J_{NH,1'}$ 5.7 Hz, H-1′), 2.37 and 2.33 (2 s, each 2 H, 2 CH_2), 2.22 and 2.09 (2 s, 9 H, 3 Ac), and 1.05 (2 s, each 3 H, 2 CH_3); ^{13}C, *δ* 199.23 and 196.17 (2 C=O), 170.51, 169.98, and 169.20 (3 $COCH_3$), 158.93 (C-1′), 133.50, 117.03, and 62.85 (allyl), 106.40 (C-2′), 51.06 and 50.13 (2 CH_2), 31.13 (-C-), 28.50 (2 CH_3), and 20.72 and 20.66 (3 $COCH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{24}H_{33}NO_{10}$: C, 58.17; H, 6.71; N, 2.83. Found: C, 57.82; H, 6.74; N, 2.60.

Allyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-*β*-D-fructofuranoside (**15***β*, 6%) had m.p. 164–166° ($CHCl_3$), $[\alpha]_D^{26}$ −8° (*c* 1, water); λ_{max}^{EtOH} 251 and 306 nm (log ε 4.13 and 4.26); ν_{max}^{KBr} 1660 vs and 1590s (C=O), and 1560 cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^1H, *δ* 10.92 (dt, 1 H, $J_{NH,1}$ 6.5, $J_{NH,1'}$ 6.5 Hz, NH), 8.07 (d, 1 H, $J_{NH,CH=}$ 14.2 Hz, =CH), 5.92 (m, 1 H, $CH_2=CH$), 5.35 (dd, 1 H, $J_{3,4}$ 9.4, $J_{4,5}$ 5.7 Hz, H-4), 5.25 and 5.06 (2 dd, each 1 H, $CH_2=CH$), 2.30 and 2.24 (2 s, each 2 H, 2 CH_2), and 0.96 (s, 6 H, 2 CH_3); ^{13}C, *δ* 200.44 and 198.25 (2 C=O), 160.64 (C-1′), 135.92, 117.04, and 63.08 (allyl), 103.15 (C-2′), 51.56 and 51.29 (2 CH_2), 31.87 (-C-), and 29.10 and 28.83 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{18}H_{27}NO_7$: C, 58.52; H, 7.37; N, 3.79. Found: C, 58.37; H, 7.20; N, 3.74.

The corresponding 3,4,6-triacetate **16***β* (94%) was a syrup having $[\alpha]_D^{26}$ −42° (*c* 1, chloroform); λ_{max}^{EtOH} 250 and 305 nm (log ε 4.05 and 4.17); $\nu_{max}^{CHCl_3}$ 1740vs (C=O, AcO), 1665s and 1660vs (C=O), and 1580sh,s cm^{-1} (C=C–NH). N.m.r. data ($CDCl_3$): ^1H, *δ* 11.31 (m, 1 H, NH), 8.12 (d, 1 H, $J_{NH,CH=}$ 14.0 Hz, =CH), 5.89 (m, 1 H, $CH_2=CH$), 5.46 (dd, 1 H, $J_{3,4}$ 7.5, $J_{4,5}$ 6.4 Hz, H-4), 5.30 and 5.20 (2 dd, each 1 H, $CH_2=CH$), 5.20 (d, 1 H,

H-3), 4.34 (dd, 1 H, $J_{5,6'}$ 3.0, $J_{6,6'}$ −11.7 Hz, H-6'), 4.15 (m, 2 H, H-5,6), 3.69 (dd, 1 H, $J_{NH,1}$ 7.0, $J_{1,1'}$ −13.9 Hz, H-1), 3.57 (dd, 1 H, $J_{NH,1'}$ 6.3 Hz, H-1'), 2.40 and 2.36 (2 s, each 2 H, 2 CH_2), 2.15, 2.10, and 2.07 (3 s, each 3 H, 3 Ac), and 1.06 (s, 6 H, 2 CH_3); ^{13}C, δ 199.10 and 196.02 (2 C=O), 179.69, 170.29, and 169.23 (3 $COCH_3$), 159.20 (C-1'), 133.45, 116.61, and 62.83 (allyl), 102.93 (C-2'), 51.25 and 50.97 (2 CH_2), 30.92 (-C-), 28.43 and 28.31 (2 CH_3), 20.60, 20.51, and 20.37 (3 $COCH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{24}H_{33}NO_{10}$: C, 58.17; H, 6.71; N, 2.83. Found: C, 57.93; H, 7.03; N, 2.62.

Glycosidation of **6** with $PhCH_2OH$ gave **17***a* and **17***β*. Benzyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-*α*-D-fructofuranoside (**17***α*, 45%) had m.p. 90–101° (from EtOH–H_2O), $[\alpha]_D^{32}$ +33° (*c* 1, ethanol); λ_{max}^{EtOH} 253 and 305 nm (log ε 4.15 and 4.26); ν_{max}^{KBr} 1660vs and 1605s (C=O), and 1595vs cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^{1}H, δ 11.00 (dt, 1 H, $J_{NH,1}$ 6.7, $J_{NH,1'}$ 6.7 Hz, NH), 8.12 (d, 1 H, $J_{NH,CH=}$ 14.3 Hz, =CH), 7.32 (m, 5 H, Ph), 4.58 (m, 2 H, OCH_2), 2.29 and 2.24 (2 s, each 2 H, 2 CH_2), and 0.97 (s, 6 H, 2 CH_3); ^{13}C, δ 197.61 and 194.54 (2 C=O), 138.52, 128.32, 127.65, and 127.43 (C_6H_5), 106.69 (C-2'), 63.01 (OCH_2), 51.01 and 50.76 (2 CH_2), 30.90 (-C-), and 28.38 and 28.07 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{22}H_{29}NO_7 \cdot H_2O$: C, 60.40; H, 7.14; N, 3.20. Found: C, 60.71; H, 7.24; N, 2.99.

The corresponding 3,4,6-triacetate **18***α* (95%) was a syrup, $[\alpha]_D^{32}$ +42° (*c* 1.1, dichloromethane); λ_{max}^{EtOH} 250 and 306 nm (log ε 4.13 and 4.25); ν_{max}^{KBr} 1665s (C=O) and 1600s cm^{-1} (C=C–NH and C=C arom.). N.m.r. data ($CDCl_3$): ^{1}H, δ 11.11 (ddd, 1 H, NH), 8.02 (d, 1 H, $J_{NH,CH=}$ 11.8 Hz, =CH), 7.20 (m, 5 H, Ph), 5.33 (d, 1 H, $J_{3,4}$ 2.1 Hz, H-3), 4.97 (dd, 1 H, $J_{4,5}$ 5.0 Hz, H-4), 4.67 (m, 2 H, OCH_2), 3.80 (dd, 1 H, $J_{NH,1}$ 7.4, $J_{1,1'}$ −14.3 Hz, H-1), 3.67 (dd, 1 H, $J_{NH,1'}$ 5.7 Hz, H-1'), 2.37 and 2.33 (2 s, each 2 H, 2 CH_2), 2.22, 2.09, and 2.05 (3 s, each 3 H, 3 Ac), and 1.04 (s, 6 H, 2 CH_3); ^{13}C, δ 198.57 and 195.54 (2 C=O), 169.87, 169.30, and 168.55 (3 $COCH_3$), 158.30 (C-1'), 136.40, 127.90, 127.30, and 126.83 (C_6H_5), 106.04 (C-2'), 62.92 (OCH_2), 50.70 and 50.41 (2 CH_2), 30.48 (-C-), 28.85 (2 CH_3), and 20.08 and 19.97 (3 $COCH_3$). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{28}H_{35}NO_{10}$: C, 61.64; H, 6.46; N, 2.57. Found: C, 61.68; H, 6.47; N, 2.27.

Benzyl 1-deoxy-1-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-*β*-D-fructofuranoside (**17***β*, 3%) had m.p. 178–180° (from EtOH–H_2O), $[\alpha]_D^{32}$ −22° (*c* 1, ethanol); λ_{max}^{EtOH} 252 and 306 nm (log ε 4.11 and 4.23); ν_{max}^{KBr} 1660s (C=O) and 1590s cm^{-1} (C=C–NH). N.m.r. data [$(CD_3)_2SO$]: ^{1}H, δ 11.09 (dt, 1 H, NH), 8.22 (d, 1 H, $J_{NH,CH=}$ 14.3 Hz, =CH), 7.43 (m, 5 H, Ph), 4.78 (m, 2 H, OCH_2), 2.42 and 2.36 (2 s, each 2 H, 2 CH_2), and 1.08 (s, 6 H, 2 CH_3); ^{13}C, δ 197.90 (2 C=O), 159.20 (C-1'), 138.91, 128.18, 127.36, and 127.17 (C_6H_5), 102.60 (C-2'), 63.03 (OCH_2), 50.95 and 50.74 (2 CH_2), 30.89 (-C-), and 28.36 and 28.09 (2 CH_3). The ^{13}C-n.m.r. data of the sugar moiety are listed in Table III.

Anal. Calc. for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 63.00; H, 6.91; N, 3.13.

Preparation of alkyl 1-amino-1-deoxy-α-D-fructofuranosides (**19–22**). — A solution of the *N*-protected glycoside (1 equiv.) in Me_2CO–H_2O (2:1) was stirred with Amberlite IRA-400 (HO^-) resin (7 equiv.) for 1 h at room temperature, then filtered. The resin was washed well with Me_2CO–H_2O (2:1), then with MeOH, the combined filtrate and washings were concentrated, and the residual aqueous solution was freeze-dried to give the glycoside. The physical constants, yields, and analytical data are summarized in Table IV. The ^{13}C-n.m.r. data of **19**, **21**, and **22** are listed in Table V.

ACKNOWLEDGMENTS

This work was supported with grants from the Consejo Superior de Investigaciones Cientificas (Project No. 129) and the Comisión Asesora de Investigación Científica y Técnica (Project No. PR84-0157-CO2-01). We thank the Instituto de Química Orgánica General, C.S.I.C. (Madrid) for the microanalyses.

REFERENCES

1 P. Borrachero Moya and A. Gómez-Sánchez, *An. Quim.*, 84 (1988) 55–59.
2 A. Gómez-Sánchez, P. Borrachero Moya, and J. Bellanato, *Carbohydr. Res.*, 135 (1984) 101–116; M. G. García Martín, C. Gasch, A. Gómez-Sánchez, M. J. Diánez, and A. López Castro, *ibid.*, 162 (1987) 181–197; A. Gómez-Sánchez, M. G. García Martín, and C. Gasch, *ibid.*, 164 (1987) 255–264.
3 R. B. Caballero, J. Fuentes Mota, and J. A. Galbis Pérez, *Carbohydr. Res.*, 154 (1986) 280–288; J. Fuentes Mota, M. A. Pradera Adrian, C. Ortiz Mellet, and J. M. García Fernández, *ibid.*, 173 (1988) 1–6.
4 L. M. Verstraeten, *Adv. Carbohydr. Chem.*, 22 (1967) 229–305.
5 J. P. Daney, *Adv. Food. Res.*, 30 (1986) 77–138.
6 A. Gómez-Sánchez, M. G. García Martín, and C. Pascual, *Carbohydr. Res.*, 149 (1986) 329–345.
7 F. García González, A. Gómez-Sánchez, M. Gómez Guillén, and M. Tena Aldave, *An. Fis. Quim.*, 67 (1971) 389–396.
8 A. Gómez-Sánchez, E. Sempere, and J. Bellanato, *J. Chem. Soc., Perkin Trans. 2*, (1981) 561–570.
9 S. B. Tjan and G. A. M. v. der Ouweland, *Tetrahedron*, 30 (1974) 2891–2897.